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ASEE/ONT Final Report

Arthur A. Morrish, NRL, Code 6522

N00014-88-J-1072
1988Introduction

In the initial research proposal submitted to ASEE/ONT it was proposed that Fourier Transform Spectroscopy (FTS), Auger Electron Spectroscopy (AES) and X-ray Photoelectron Spectroscopy (XPS) be used investigate the process of oxidation. These techniques would also be used to characterize the oxides that form on the surface of metals and metallic films. This surface oxidation process can lead to reduction of the infrared reflectance of the surface, changes in the electrical transport properties of the metal, and changes in the passivity of the metals, which prevents corrosion. The process by which this surface oxidation occurs and its effects on various materials is of interest to the Navy.

The project was envisioned as being comprised of two related efforts, and they would proceed roughly simultaneously. Phase one was to develop the infrared devices necessary to make in-situ infrared emission measurements in a gaseous environment. In Phase two, measurements of the oxidation properties of various metallic films would be made via XPS and AES. These measurements would be related to infrared data if possible. Since this project resulted in several papers, conference presentations and an invention disclosure, only a summary of the work will be presented here. A publication list is included for more detailed information.

Phase one: Infrared Devices and Measurements

In the early portion of this phase of the project these are the major tasks that were undertaken and completed: set up, and become familiar with FTS and peripherals, write initial operating programs for FTS and undertake a literature search on Emission and Absolute Specular Reflectance FT-IR. Since surface oxidation

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of most materials results in a change in the infrared reflectance of the material, an effort was made to determine whether the absolute specular reflectance of these materials could be measured with a commercial variable angle, absolute specular reflectance device. Figure 1 demonstrates the method for making these measurements with a "V-W" type of optics. Since the surface oxidation layer can be very thin, the device must be able to measure small changes in the infrared reflectance. An absolute accuracy of 0.1% was determined to be acceptable. As delivered, the commercial device was incapable of meeting the absolute accuracy requirements. This was largely due to drift of the beam spot on the detector. The drift occurred because of small inaccuracies in repositioning the device when changing from the "V" to the "W" mode. The author and his supervisor, Dr. Snail, then redesigned and modified the commercial device to improve the accuracy and reproducibility of the device when doing absolute specular reflectance at variable angles. Figure 2 shows the modified device. This work resulted in paper #1 in the publications list. At this time it was determined that absolute specular reflectance was not going to provide the kind of information and accuracy that was needed. The results of the literature search indicated that infrared emission spectroscopy might provide the kind of data required.

Basically, infrared emission spectroscopy measures the intensity of infrared radiation that is emitted from a hot surface over a range of wavelengths, usually from 2 to 20 microns. Changes in the IR emission spectrum of materials undergoing surface oxidation should be readily observable. Toward the middle of the first year of the project, design of a direct emission accessory for an FTS instrument began. The design for the accessory consisted of a blackbody reference, a heated sample mount and a null compartment so that the effect of self-emission errors from the instrument could be determined. Water cooling is employed throughout the accessory to minimize errors introduced from self-emission. The accessory is also

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designed to allow reactive gases to flow over the heated sample. In this fashion time dependent, in-situ measurements can be made of the effect of oxide formation (or other compounds) on the emittance of metal films and metallic surfaces. Both the sample heater and the blackbody can achieve temperatures of 600° C. The temperatures are measured and controlled by platinum resistance thermometers and controllers which are accurate to 0.1° C. The blackbody has an emittance of > 0.94 as specified by the manufacturer. Figures 3 and 4 show the sample accessory and how it interfaces with FTS.

Construction of the accessory began in the first quarter of 1987. The fabrication of the device was completed in the third quarter of 1987. Testing and assembly of the components was undertaken during the third and fourth quarters of 1987. Full scale testing started in the fourth quarter of 1987 and is continuing at present. This device resulted in an invention disclosure which was filed with the Naval Research Laboratory's Patent Office in the first quarter of 1988. The device is also described in paper #5 in the publications list. It is planned that the first experimental work can begin on this accessory in the very near future.

Phase Two: XPS and AES Analysis

In Phase Two the surface sensitive techniques of XPS and AES were employed. These techniques were used to analyze the chemical structure, purity and oxidation resistance of two metallic films developed for passivating other metal surfaces. The films are titanium nitride (TiN_x) and molybdenum silicide ($MoSi_x$).

Concurrently with Phase One, several tasks began in Phase Two. These included becoming familiar with the XPS instrument belonging to NRL Surface Chemistry and beginning regular XPS analyses of the thin film samples generated by our thin films group. Also, in the first quarter of 1987, training began and was successfully completed to qualify as an operator of the NRL

Scanning Auger Multiprobe (SAM) system. This training required 30 hours of study and hands on experience. After the training period was completed continuing SAM analysis began.

Titanium nitride was the first material which was studied. Initially an attempt was made to correlate the microstructure and composition of sputtered titanium nitride films with their electrical and optical properties. A set of TiN_x films were reactively sputtered onto quartz substrates at temperatures between 140 and 850° C. Quartz substrates were used initially, because they provide a simple model substrate that does not interact with the film. Metal substrates were used later in the project. The samples were characterized by x-ray absorption fine structure (EXAFS) and chemically characterized via XPS. Briefly, it was determined that neither the film's crystalline structure nor its stoichiometry changed significantly over the entire range of temperatures. However, the percentage of impurities that are were found in the materials did decrease with increasing temperature. This observation correlated well with the observed decrease in electrical resistivity and increase in infrared reflectivity of the films deposited at higher substrate temperatures.

It was also shown that oxygen and carbon, which constitute the majority of the impurities, appeared to be segregated to the void pockets and/or grain boundaries. This effect could be explained by either an increase in grain size, or decrease in void fractions in the material, as a function of increasing temperature. Table #1 shows the changes in composition as a function of temperature. Further discussion of this experiment can be found in paper #2 in the publications list.

In a related experiment the effects of grain size on the oxidation kinetics of sputtered titanium nitride films were investigated. In applications where films are exposed to oxygen at elevated temperatures, it is important to understand their oxidation kinetics in order to predict the resistance of the films to oxidation. In this study polycrystalline TiN films were

used to determine the effects of grain size on their rate of oxidation. Several studies have shown that diffusion down grain boundaries is enhanced over that of the crystalline lattice. If the grain size in a polycrystalline film is sufficiently small, then diffusion along the grain boundary surfaces may be the dominant reaction mechanism and therefore control the oxidation rate.

The TiN films were reactively sputtered onto sapphire substrates. A variety of grain sizes were obtained by varying the temperature of the substrate on which the films were deposited. The temperatures ranged between 140° and 850° C. A sample of single crystal TiN on MgO was used for a comparative endpoint. After deposition, grain sizes were determined by X-Ray Diffraction (XRD), and the compositional analysis was made using a PHI 660 Scanning Auger Multiprobe (SAM). Following the XRD and SAM analyses selected samples (deposited at 650° C and 850° C) were oxidized at 200° C for 24 hours. Following the oxidation the analyses were repeated. The samples were then oxidized at 300° C for 24 hours and analyzed a final time.

In summary, the study attempted to relate the oxidation kinetics of sputtered TiN films to their as deposited grain size. The results demonstrated that grain boundary diffusion is predominant in films with an average grain diameter of 545 angstroms or less, this being all films deposited at 650° C or less. It also showed that the rate of oxidation for such films is significantly higher than for crystalline material. However, for films deposited at temperatures high enough to produce a preferred orientation of the grains, 850° C and above, the oxidation rate is not significantly different than that of the crystalline material. This indicates that bulk diffusion through the oxide layer is the rate-determining step in those films. Figure 5 illustrates the relationship between the oxide thickness produced on the films, which is directly related to oxidation rate, and the deposition temperature which controls the grain size of the film. A more detailed discussion of this work may be

found in paper #4 in the publications list.

A series of experiments similar to those carried out on TiN began on Molybdenum Silicide (MoSi_2). MoSi_2 is a refractory material with a high resistance to oxidation, which made it of particular interest to our group. All of the films were prepared in a similar fashion. They were deposited in an Rf sputtering system using separate molybdenum and silicon targets.

Samples were deposited at a variety of composition ratios of molybdenum to silicon ranging from 0.15 to 1.5. The films were deposited at substrate temperatures ranging from ambient to 750°C .

The film adhesion generally improved with increasing substrate temperature, and also with increasing molybdenum content. The thermal stability of the films was determined by subjecting each of the films to 24 hour anneals at temperatures ranging from 240° to 560°C . For all of the films except those with a molybdenum to silicon ratio of approximately 0.5, oxidation occurred at the lowest anneal temperature. The films with a composition close to MoSi_2 showed no visible signs of oxidation for temperatures less than 460°C . It was found that a surface layer of SiO_2 is present with a molybdenum rich layer directly behind it. This occurs due to the relatively greater stability of SiO_2 as compared to the primary oxide of molybdenum MoO_3 . The surface oxide layer acts as a diffusion barrier, inhibiting the further oxidation of the film. Figure #6 is an XPS depth profile of an MoSi_2 film deposited at ambient substrate temperature.

Other investigations including some work on correlating the levels of impurities in sputtered molybdenum silicide films with optical and transport properties is proceeding. Also a study on the effects of grain boundaries on the transport properties of these films is underway.

The next stage in the investigation of the oxidation process in relation to the materials discussed above indicated that the types of oxidation experiments that could be done at NRL has been completed. Their results indicated that a more sophisticated

method of subjecting the films to a stressful or oxidizing environment was necessary. To this end a co-operative effort is being undertaken with another Navy lab (the Naval Air Propulsion Center (NAPC)), to produce a variety of oxidized metal and metal film samples for us. Several batches of samples have been delivered to NAPC. Analytic work has begun on some of the samples, and will proceed as more are returned. Another series of samples is being developed for testing later in the year if money allows.

Conclusion

In summary the work done under this post-doctoral fellowship helped established the error limits of a commercial variable angle reflectance accessory. It supported the work necessary to design, construct and begin preliminary testing of a novel device which measures the infra-red emission of materials under exposure to a variety of environments. Work done under this fellowship has also contributed to the understanding of the effects of oxidation, grain size, deposition parameters and impurity levels on the optical and electrical transport properties of TiN and MoSi₂ films. This accumulated work has resulted in the papers listed below as well as numerous presentations, both formal and informal.

Publications accepted during 1986-87:

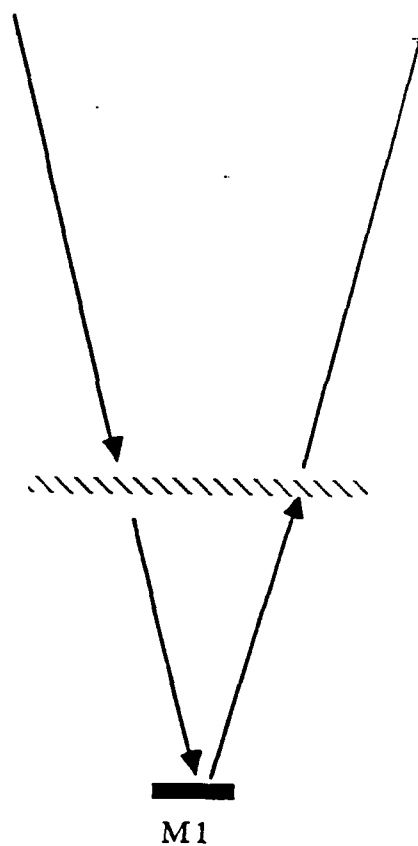
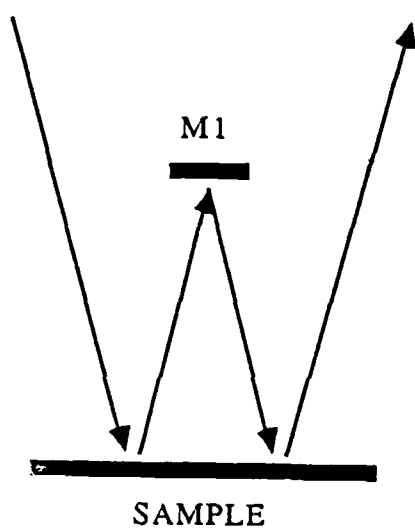
1. Snail, K. A., Morrish, A. A., and Hanssen, L.; "Absolute Specular Measurements in the Infrared", Proceedings of August 1986 SPIE conference, San Diego, CA
2. Thorpe, T. P., Elam, W. T., and Morrish, A. A., "Correlation of Microstructure and Composition of Sputtered Titanium Nitride Films with Electrical and Optical Properties", to be published in Journal of Vacuum Science and Technology A, July/August, 1987
3. Thorpe, T. P. and Morrish, A. A., "Examination of Molybdenum Silicide as a High Reflectivity Coating in Adverse Environments", to be published in proceedings of IRIS Specialty Group on Infrared Materials", June, 1987
4. Thorpe, T. P., Morrish, A. A., and Qadri, S. B., "Effect of Grain Size on Oxidation Kinetics of Sputtered TiN Films", to be published in Journal of Vacuum Science and Technology
5. Snail, K. A., Hanssen, L. M., and Morrish, A. A., "New Optical Systems for the Measurement of Diffuse Reflectance and Emission", presented at the Workshop on Optical Properties Measurement Techniques, October 27-29, Ispra Italy, Sponsored by the Committee of European Communities

Table I. Relative proportions of titanium in TiN_x films bound to major film constituents, as determined by XPS measurements. Deposition temperatures are as indicated.

Elements	Deposition temperature		
	140 C	570 C	
Ti-N	52.5 %	54.7%	54.6%
Ti-R ₂	25.1%	25.5%	25.6%
Ti-O ₂	22.7%	19.7%	19.8%

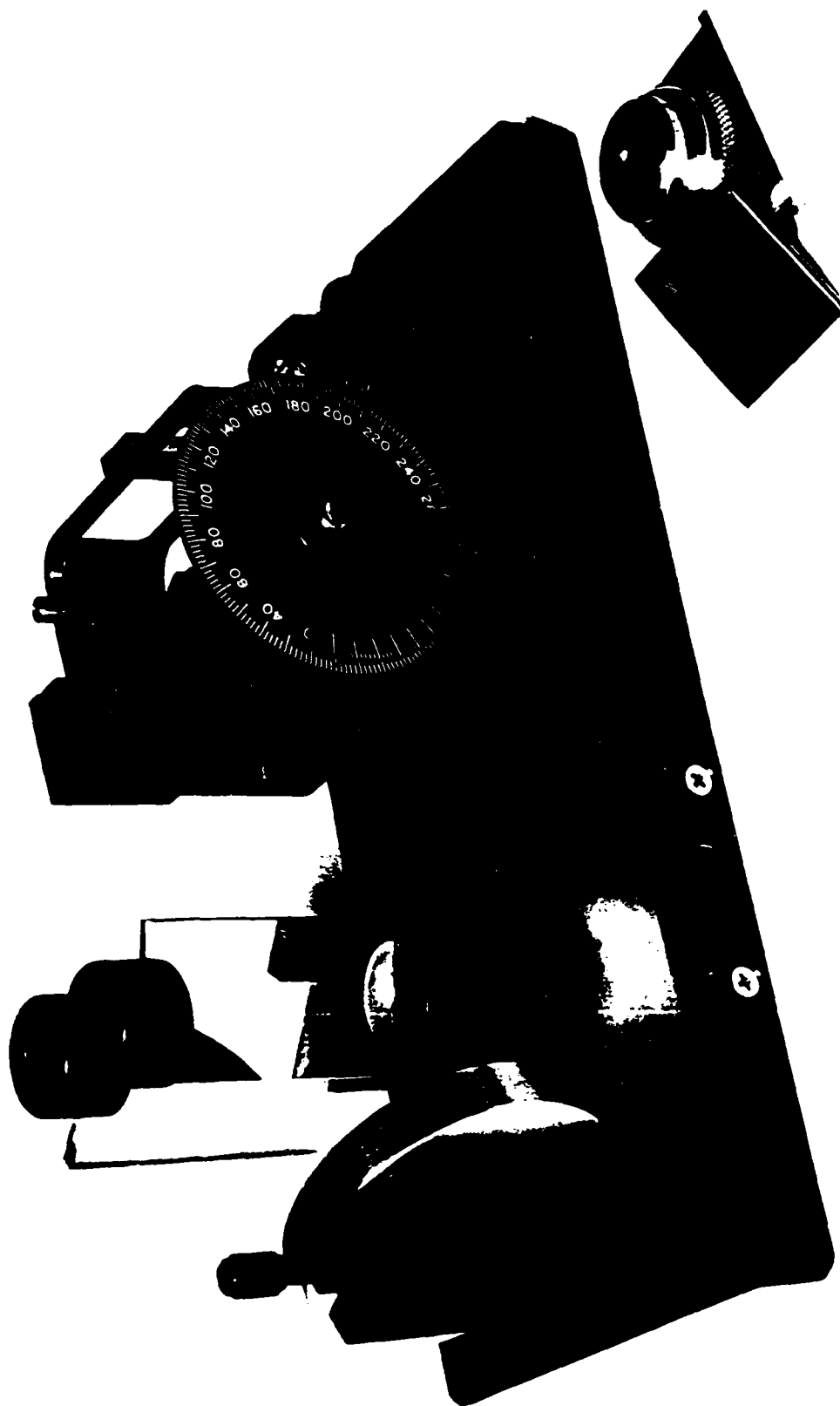
Figure 1

STRONG'S "V-W" OPTICAL SYSTEM



$$\frac{R(W)}{R(V)} = R^2$$

Figure 2



DIRECT EMISSION ACCESSORY

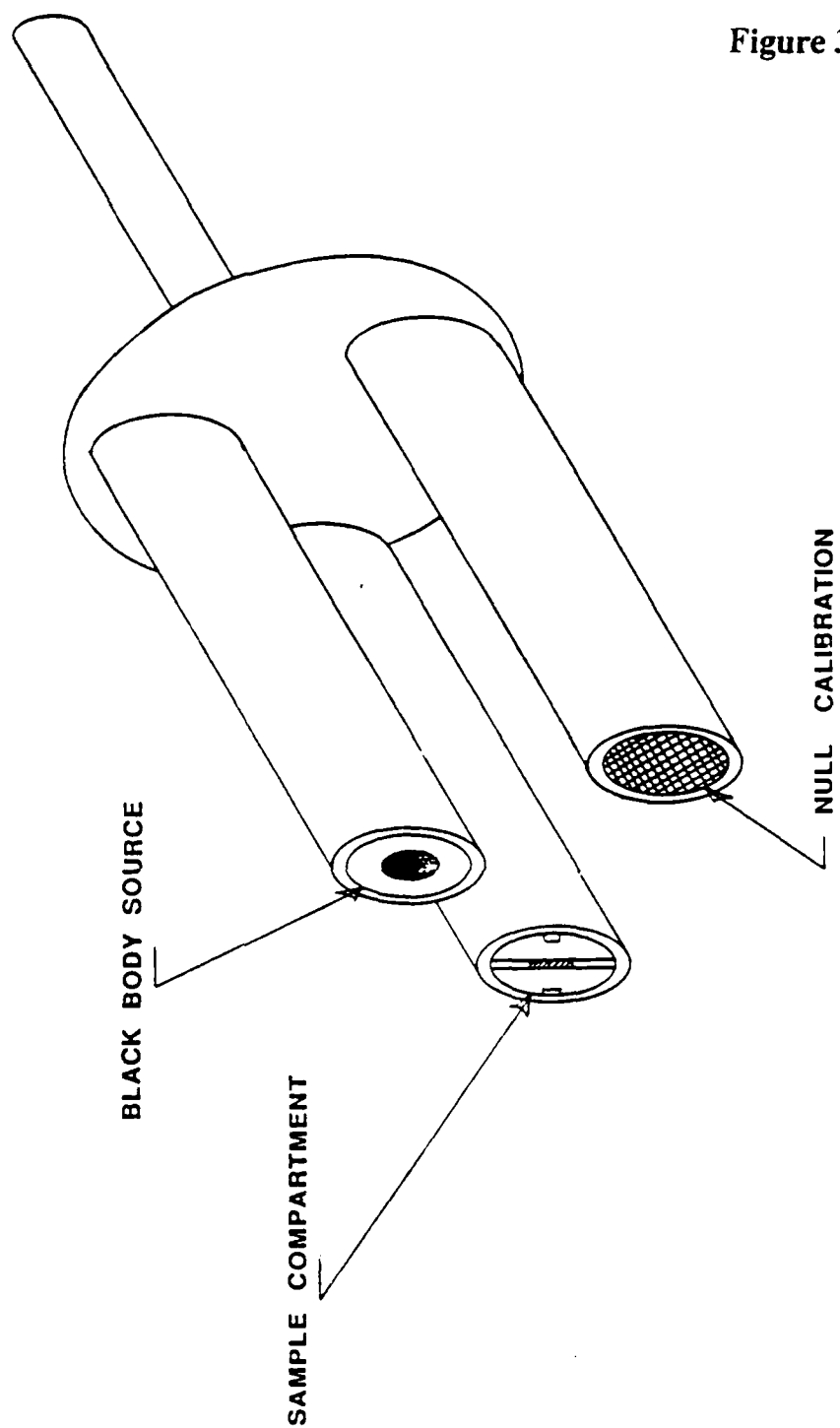


Figure 3

INTEGRATION OF EMISSION MEASUREMENT DEVICE INTO NRL IR-LOBS MEASUREMENT FACILITY

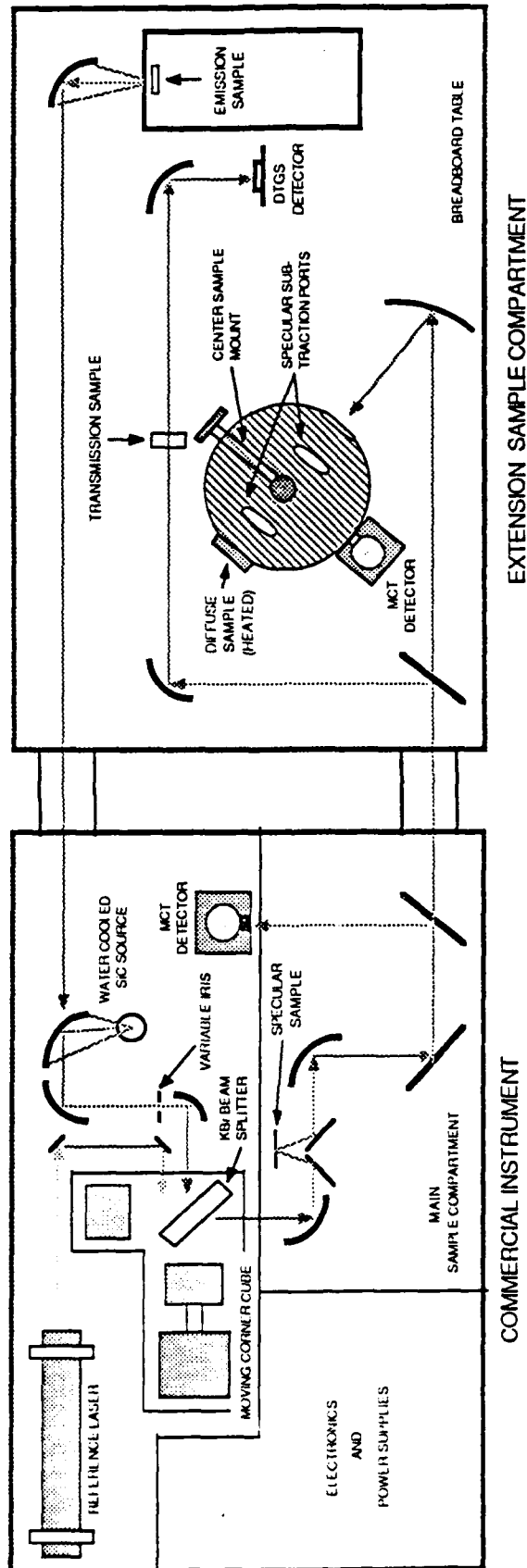
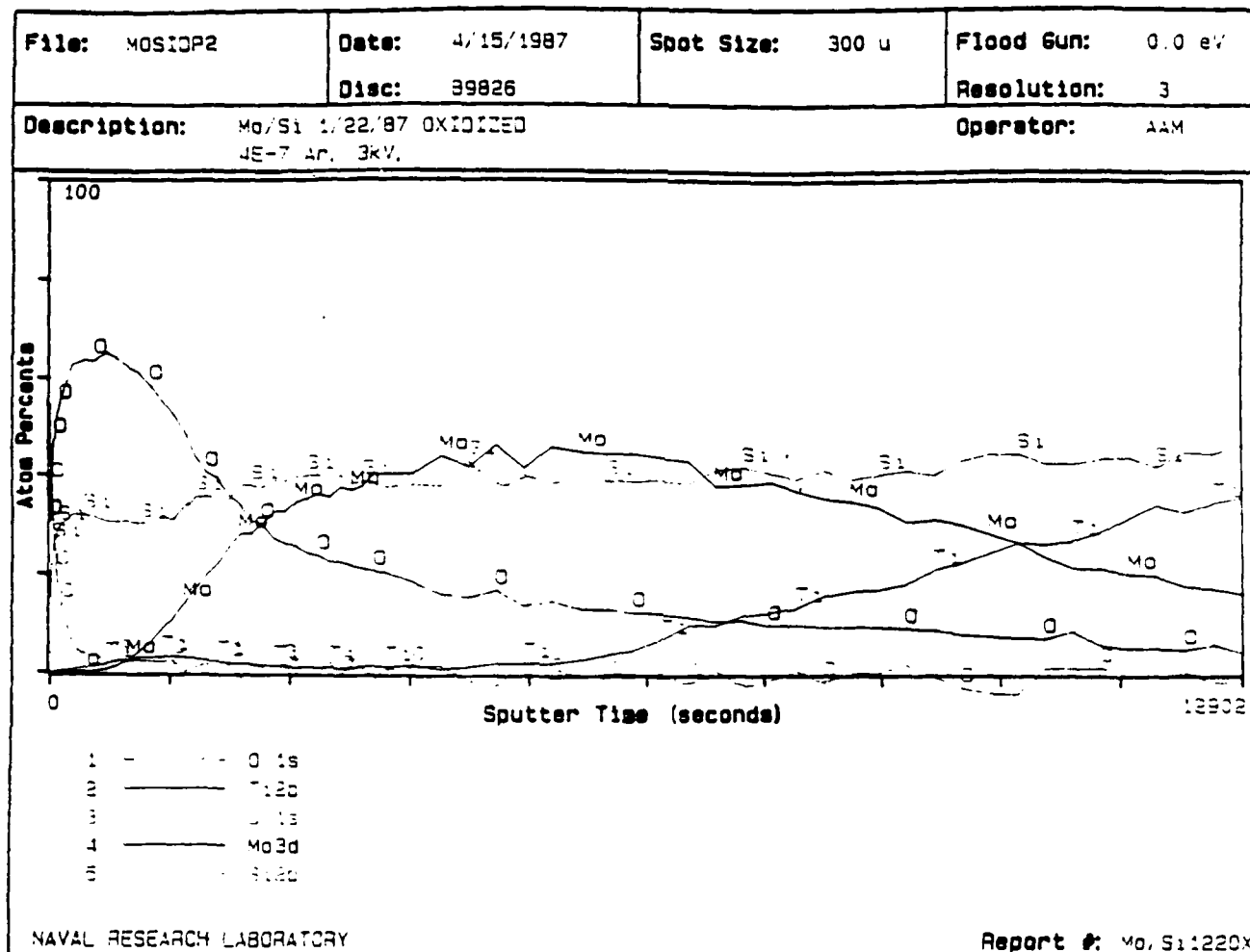


Figure 4

Figure 5

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XPS depth profile of MoSi_2 film after exposure to air at 560°C for 24 hours.

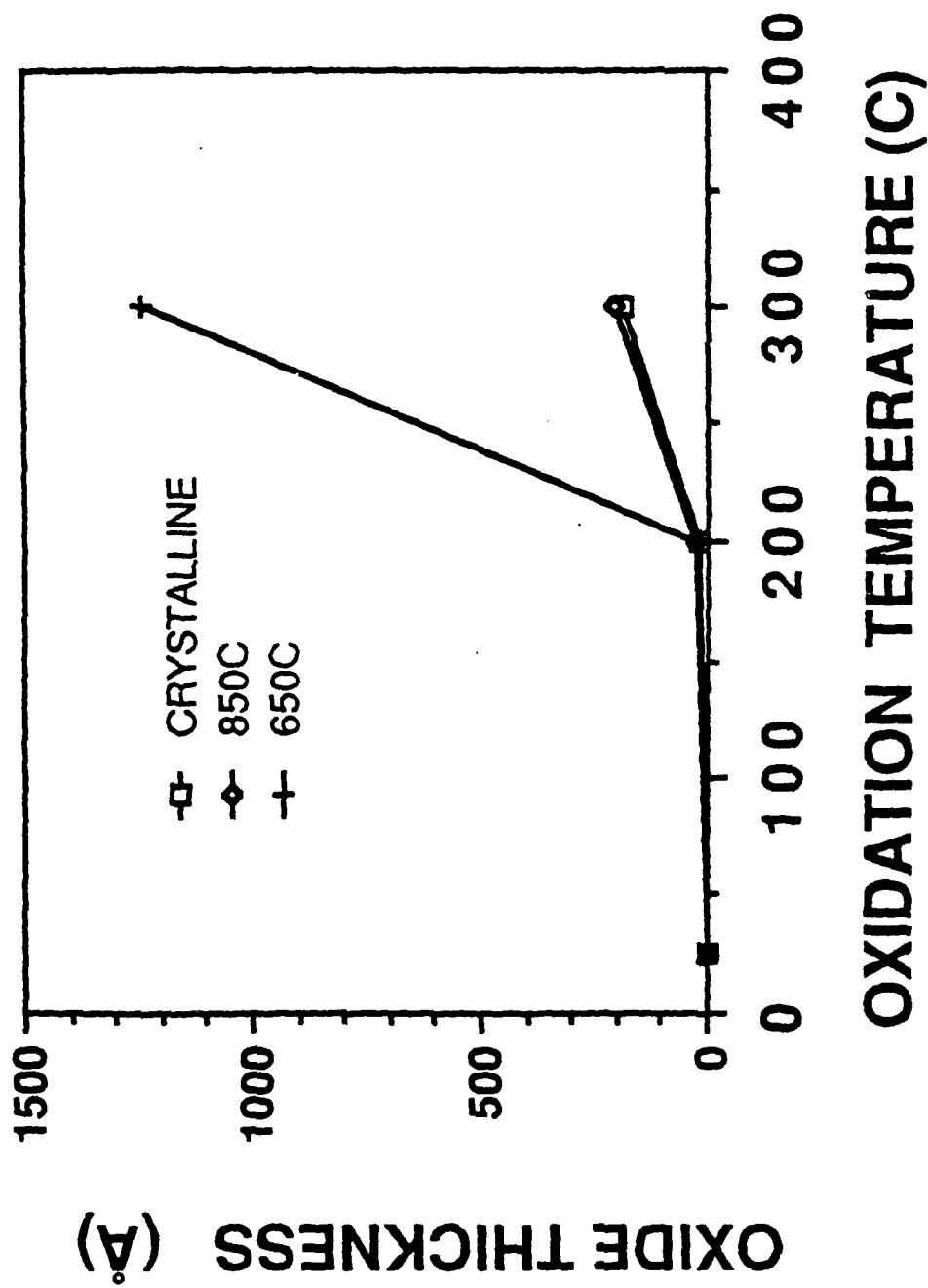


Figure 6

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